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# Crystal structure of mixed-layer minerals and their X-ray identification: New insights from X-ray diffraction profile modeling

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**Abstract:** Modeling of experimental X-ray diffraction (XRD) patterns represents the optimum approach to the structure determination of mixed-layer structures (MLSs) that are commonly found in natural clay-rich samples. This approach allows for a detailed structural characterization of both pure and mixed-layer clay phases and for a semi-quantitative phase analysis in complex mixtures. The two informations are essential to gain new insight into the actual nature of reactions taking place in geological environments. Significant new findings obtained at different scales (from that of the particle to that of the elementary layer) on the actual structure of MLSs by modeling XRD profiles are reported.

**Keywords:** X-ray diffraction, layered minerals, mixed-layering, interstratification, simulation, crystal structure, crystal chemistry, expandable layers, order-disorder

## 1. Introduction

Mixed-layer structures (MLSs) are remarkable examples of order-disorder observed in natural and synthetic lamellar crystals. They consist of the alternation of layers exhibiting contrasting structures and compositions in variable proportions. Mixed-layering (or interstratification) has been widely recognized in natural and synthetic species such as layer silicates, layer manganates, hydrotalcites and synthetic layered double hydroxides, layer oxides in general, sulphides, intercalated graphites, ...

In natural environments, interstratification is especially widespread among clay minerals (phyllosilicates) which differ in the type of interstratified layers and in their stacking sequences. Because of the reactivity of the frequently interstratified expandable layers and of their resulting ability to evolve as a function of physico-chemical conditions, these MLSs have drawn special attention for decades in an effort to use them as indicators of paleo-conditions (and more especially of temperature paleo-conditions) and/or of reaction progress<sup>1,2</sup>.

To establish these interpretations on scientifically sound bases, a detailed structural characterization of the MLSs is essential so as to assess the nature of the elementary layer types, to determine the reaction mechanisms, and, ultimately, to determine thermodynamic data relevant to these systems and possibly the kinetic effects affecting these reactions. X-ray diffraction (XRD) has been the preferred method used to determine the actual structure of these MLSs.

However, because of their finely divided character which is likely related to the abundance of stacking “defects”, represented by the stacking of different layer types, and of the resulting non-periodicity, interpretation of XRD effects from MLSs cannot be satisfactorily achieved with conventional XRD methods such as single crystal

diffraction and/or Rietveld structure refinement using powder diffraction data. This impossibility has led to the development of specific algorithms for the calculation of diffraction effects arising from MLSs.

In particular, a matrix formalism has been developed to describe the intensities of basal ( $00\ell$ ) and  $hk\ell$  reflections diffracted by a set of crystals containing different layer types<sup>3-13</sup>). Another approach, which is based on the direct summation of the contributions to diffracted intensity coming from waves scattered by all possible layer subsequences in the mixed-layer crystals, was also developed for calculation of XRD patterns from MLSs<sup>14,15</sup>). Ideally, identification of MLSs is derived from the comparison of experimental XRD profiles with those calculated from a structure model. The optimum fit to the experimental data is obtained usually by a trial-and-error procedure.

Recently, the use of these time- and effort-consuming techniques has developed significantly and resulted in major improvements in the understanding of the actual structure of these defective structures. The present review will try to describe the progress that arose recently in the description of the MLSs. The discussion will focus specifically on the description of intra-crystalline defects, on the stacking sequences within MLSs, and on the structure of elementary layers.

## **2. Background**

### **2.1 Different types of MLSs**

Two main categories of MLSs can be singled out depending on the actual distribution of interstratified layer types. The first type of MLSs corresponds to regular structures in which different layer types alternate periodically along the axis perpendicular to the layer plane ( $c^*$  axis). These MLSs have often been given mineral names as they have strictly periodic structures, and as they are often considered as distinct phases. Chlorite and corrensite are two examples of such structures that can be described as regular talc-brucite and chlorite-smectite MLSs, respectively.

In the second type of MLSs, the different layer types either alternate at random or tend to some sort of ordering (avoiding the existence of pairs of the minor layer type) or segregation (clustering layers of a given type). In this case and if interstratified layers have significantly different thicknesses and structures, resulting peak positions do not obey the Bragg's law but form a non-rational series ( $d_{001} \neq \ell \times d_{00\ell}$ ) leading to an apparent lack of physical meaning for the observed peak positions. This type of MLSs will be used preferentially in the following discussion, in particular because of the interest in the structure of "illite-smectite" MLSs which has been sustained for decades.

The second type of MLSs also includes structures in which the respective thicknesses of interstratified layers are multiple of each other (e.g. chlorite-serpentine MLSs). In this case, the positions of basal reflections corresponding to the MLS form a rational series. The identification of the interstratified character of the structure thus requires a more detailed analysis of peak position, profiles (especially width) and relative intensities for different reflections.

Finally, the second type of MLS includes structures in which interstratified layers have about the same thickness but distinct structures. In this case only the positions of non-basal reflections are affected. These reflections form non-rational series as basal reflections for MLS in which interstratified layers have significantly different thicknesses and structures. Within this last type of MLS, additional variety can arise from the possible incommensurability of the interstratified layers.

## 2.2 Structure characterization of MLS and usual identification methods

A complete identification of MLSs requires the determination of the number and nature of the different layer types and their stacking sequences (including the size of the coherent scattering domains). Structural characterization of the elementary layers consists in determining their unit-cell parameters and the atomic coordinates and occupancies of the various sites.

To define layer stacking sequences, two essential sets of parameters are needed. Relative proportions of the various layer types ( $W_i$ ) make up for the first one, whereas the layer stacking mode represent the second essential parameter. Layer stacking mode is defined statistically by the probability for a B-type layer to follow an A-type layer (junction probability  $P_{AB}$ ). This concept of interaction between layers was first introduced by Jagodzinski<sup>16)</sup> and the extent of these interactions is commonly characterized with the Reichweite parameter ( $R$ ). However, for a given Reichweite value, a variety of junction probabilities may be defined ranging from the physical mixture ( $P_{AA} = 1$  whatever  $W_A$  for  $R = 1$ ) to the maximum possible degree of ordering (MPDO,  $P_{AA} = 0$  if  $W_A < 0.5$  for  $R = 1$ ). A complete description of the statistical parameter defining layer stacking sequences may be found in various texts<sup>12,15,17)</sup>.

Because of the wide and sustained interest for illite-smectite MLSs, several simplified method have been proposed over the years for their identification<sup>18-23)</sup>. These methods are essentially based on peak migration curves which link the position of a given reflection (or of a given set of reflections) to the composition (relative proportion of the different layer types) of the MLS. The curves were obtained from XRD patterns calculated using either Newmod, developed by Reynolds, or the program based on the matrix formalism developed by Watanabe. The intensity ratio between some of these reflections, or between reflections and “background”, is occasionally used as an additional criterion to estimate the relative contents of the different layer types in these MLSs.

Despite their wide use, these simplified identification methods present major drawbacks. The first and essential one is the lack of direct comparison between experimental and calculated patterns, which is intrinsic to the approach. As a result, there is no possibility to assess the validity of the identification by using a parameter measuring the “goodness of fit” as in usual crystallographic studies. When experimental XRD patterns are directly compared to those calculated on the basis of the performed identification it is clear that peak position is not a valid criterion for MLS structure characterization<sup>24)</sup>. Another essential drawback of these methods comes from the use of a unique XRD pattern for identification purposes, which does not allow the validation of the proposed identification by independent XRD measurements on the same sample submitted to different treatments (see below the description of the multi-specimen method).

In addition, the profiles of the diffraction lines, which are strongly affected by interstratification effects, are not taken into account by these peak-position methods. Additional drawbacks of these methods come from limitations of the programs used to calculate diffraction effects arising from MLS, or from the limited range used for variable parameters in order to (over ?) simplify the identification process. Intrinsic limitations of the programs include for example their inability to calculate diffraction effects from multi-component MLSs. Essential adjustable parameters which were insufficiently varied include the size of the coherent scattering domains as the calculations are most often restricted to a single mean value, and junction probabilities. Most methods include indeed calculations for randomly interstratified MLS ( $R = 0$ ,  $P_{AA} = W_A$ ) and for the sole MPDO

case for higher values of the Reichweite parameter.

### **2.3 Multi-specimen method for XRD identification of MLSs**

In contrast to most usual MLS identification methods, the multi-specimen method requires recording XRD patterns for each sample after different treatments (e.g. Ca-saturated in air-dried and/or ethylene-glycol (EG) solvated states, and/or Na-saturated in air-dried and/or ethylene-glycol solvated states). For the same sample, XRD patterns usually differ significantly after these treatments because of the contrasting hydration/expansion properties of expandable layers. It is then possible to draw additional constraints on the actual structure of the different minerals present.

The method itself consists in comparing directly experimental XRD profiles to those calculated from a structure model, and the optimum agreement between experimental and calculated XRD patterns is obtained by a trial-and-error procedure. Such structure models include for each MLS, the number (not limited to 2), the nature and the proportions of the different layer types and a statistical description of their stacking sequences (Reichweite parameter and junction probabilities). The different treatments may change the thickness and the scattering power (nature, amount, and position of interlayer species) of the swelling interlayers but not the distribution of the different layer types. A consistent structure model is thus obtained for one sample when the stacking sequences of the different layer types obtained from all experimental XRD profiles of the same sample are nearly identical. In addition to these structural parameters, relative contributions of the various phases (including MLSs) to the different XRD patterns recorded for the same sample must be similar for polyphasic clay parageneses<sup>24,25</sup>.

By constraining the structural characterization of a given sample from different experimental XRD patterns, the multi-specimen method allows overcoming one major intrinsic limitation of the XRD identification of clay minerals. This limitation arises from the strong tendency of XRD to average structural parameters describing the periodicity of crystals. The resulting low sensitivity of XRD to variation in local disorder can in particular allow for the existence of several structure models giving rise to similar diffraction effects for a given set of experimental conditions. To determine the actual structure model, additional constraints obtained from the analysis of different XRD patterns obtained from the same sample after different treatments are thus essential<sup>25,26</sup>. In addition, this method allows for a semi-quantitative phase analysis of the clay fraction including both discrete and mixed-layer clay phases in addition to the detailed structural characterization of these different components.

## **3. Recent developments and new insights into the actual structure of mixed-layers**

### **3.1 Intra-crystalline defects**

Until recently, structure models of MLSs used for the calculation of XRD profiles describe coherent scattering domains (CSDs) limited to a few layers. These models describe well the high-angle region of the experimental XRD patterns but often fail in the low-angle region ( $2\theta < 4-6^\circ 2\theta$  CuK $\alpha$ ). Usually, the calculated intensity in low-angle region is much higher than the one determined experimentally. On the other hand, simulation of experimental small angle X-ray scattering (SAXS) data obtained on related samples commonly indicate the presence of much thicker CSDs.

In an effort to reconcile the results from both methods, Plançon proposed recently a model for the simulation of experimental XRD patterns in which particles or megacrystals are significantly thicker than crystals (or CSDs)

used in the common XRD models<sup>13)</sup>. These particles contain layer types identical to those in the usual XRD model. Their relative proportion and their stacking sequences are also identical to those in the usual models. However, adjacent layers may be shifted with respect to each other along the  $c^*$  axis according to an adjustable probability. As a result, the apparent CSD size decreases with increasing  $2\theta$  angle and XRD patterns calculated according to this new model exhibit a significantly lower scattered intensity over the low-angle region as compared to the usual XRD models.

However, this model appears to lead to non-negligible discrepancies between the basal reflection positions and intensities calculated in the high-angle region as compared to the usual XRD models. To overcome this problem, an improved model which describes the degree of coherency within megacrystals crystals (or CSD's) has been proposed recently<sup>27)</sup>. This model allows reproducing diffraction features in both high and low-angle regions of experimental XRD patterns.

### 3.2 Outer surfaces of crystals

None of the algorithms routinely available to simulate XRD patterns of MLSs can account for the possibility that in natural environments the structure and composition of surface layers of crystals may differ from those of "core" layers. However, the knowledge of the outer surface layer (OSL) nature is useful to understand better surface properties of MLSs and/or to derive constraints on their growth conditions. For example, according to high-resolution transmission electron microscopy, illite crystals may terminate on a kaolinite layer<sup>28)</sup> whereas kaolinite crystals may have pyrophyllite or smectite layers as surface terminations<sup>29)</sup>.

Alternative algorithms were recently proposed to allow determining the nature of OSLs in MLSs from the simulation of XRD patterns<sup>30-32)</sup>. In particular, Sakharov et al.<sup>32)</sup> showed that among the usual MLSs found in natural samples, the most significant effects were calculated for those containing elementary chlorite layers. For chlorite samples relative intensities of the odd reflections depend not only on the distribution of Fe in the chlorite structure over the 2:1 and 0:1 layers, but also on the nature of the OSLs. For the two samples they investigated, brucite sheets were present on the crystal outer surfaces. However, the comparison of the OSL nature determined from XRD profile modeling with that deduced from direct observations using electron or atomic force microscopies (e.g.) remains essential for MLSs because similar diffraction effects may be obtained by varying structural and chemical parameters of the MLS on the one hand and the OSL nature on the other.

Sakharov et al.<sup>32)</sup> also showed that for periodic structures containing only one layer type, the influence OSLs may be predicted from simple calculations, and is independent of the scattering power of the OSL. Such a prediction is not possible for MLSs.

### 3.3 Natural occurrence of multi-component MLSs

Even though multi-component (3- but also 4-component) MLSs have been seldom described in the wealth of literature devoted to the structural characterization of these minerals, such multi-component structures are most likely overwhelmingly present in natural samples. All recent studies which were performed with calculation algorithms allowing the calculation of their XRD patterns have indeed led to the identification of MLSs that include more than two components especially as the result of the contrasting swelling/hydration behaviors of expandable layers<sup>24-26,33-39)</sup>.

For example, Ferrage et al.<sup>40)</sup> have shown on pure smectite samples that heterogeneity rather than

homogeneity is the rule for smectite hydration, even when working with homoionic samples under controlled relative humidity (RH). These authors studied the hydration of the <1  $\mu\text{m}$  size fraction of SWy-1 source clay (low-charge montmorillonite) by modeling XRD patterns recorded under controlled RH conditions on Li-, Na-, K-, Mg-, Ca-, and Sr-saturated specimens. The quantitative description of smectite hydration they proposed from experimental XRD pattern modeling is consistent with previous reports of smectite hydration. However, the coexistence of smectite layer types exhibiting contrasting hydration states was systematically observed. This hydration heterogeneity can be characterized qualitatively with the standard deviation of the departure from rationality of the  $00\ell$  reflection series ( $\xi$ ), which, in their study, is systematically larger than 0.4 Å when the prevailing layer type accounts for ~70% or less of the total layers (~25% of XRD patterns examined). In addition, hydration heterogeneities are not randomly distributed within smectite crystallites, and models describing these complex structures involve a minimum of two distinct contributions, each containing different layer types that are randomly interstratified. As a result, the different layer types are partially segregated in the sample.

### 3.4 Layer stacking sequences in MLSs

The existence of such partial segregation, or partial ordering, has been frequently reported also in recent studies of natural MLSs performed with the multi-specimen method<sup>24-26,33-39</sup>). Such high frequency of natural MLSs exhibiting junction probabilities different from the usual  $R = 0$  and MPDO cases clearly demonstrates that XRD profile modeling is the unique tool that can provide an accurate structure characterization of MLS as peak migration curves are not available for junction probabilities different from the “ideal” cases envisaged (MPDO, random interstratification, ...).

The use of XRD profile modeling has also led to the description of “unusual” MLSs, such as randomly interstratified illite-smectite MLSs with a high illite content (~70% illite), which are characterized by broad and poorly defined contributions to the diffracted intensity. This specific diffraction fingerprint, without any significant maximum in the low-angle region, likely hinders the recognition of such highly illitic randomly interstratified MLSs in natural samples and is most likely responsible for their seldom description in works based on the position of diffraction maxima.

### 3.5 Detailed structure determination of elementary layers

Quantitative description of the MLS diffraction patterns which has been increasingly used over the last few years has not only allowed a more realistic description of mixed-layer crystals but has also brought significant new insights in the structure of individual layers. For example, new structure models have been proposed for bi-hydrated smectite layers<sup>41</sup>). According to this improved model, interlayer cations are located in the mid-plane of the interlayer whereas H<sub>2</sub>O molecules are scattered about two main positions according to Gaussian-shaped distributions.

This configuration allows reproducing all  $00\ell$  reflections with a high precision, with only one new variable parameter (width of the Gaussian function). In addition, the proposed configuration is consistent with those derived from Monte-Carlo calculations and allows matching more closely the amount of interlayer water that can be determined independently from water vapor adsorption/desorption isotherm experiments. In addition, the proposed configuration of interlayer species appears valid for both dioctahedral and trioctahedral smectites exhibiting octahedral and tetrahedral substitutions, respectively. This model thus allows the definition of a unique

interlayer configuration for all expandable 2:1 phyllosilicates.

In addition to the location of interlayer species, XRD profile modeling has allowed the refinement of structural parameters such as the layer thickness corresponding to the different layer types for various interlayer cations and RH values. In particular, it has been possible to quantify the dependence of layer thickness on the cation ionic potential ( $\frac{V}{r}$ ,  $v$  = cation valency and  $r$  = ionic radius) and on RH, and to link the increase observed with increasing RH to the increased amount of interlayer H<sub>2</sub>O molecules in both mono- and bi-hydrated smectite layers.

#### 4. Conclusion

Modeling of experimental XRD patterns represents the optimum, and at present the sole, quantitative method allowing the determination of MLS structure. For a few years, modeling of experimental XRD patterns has been successfully used to describe, with a trial-and-error fitting procedure, the actual structure of both synthetic and natural samples, including complex parageneses found, for example, in diagenetically altered shales samples. Such detailed modeling of experimental XRD data allows for a semi-quantitative phase analysis of the clay fraction including both discrete and mixed-layer clay phases in addition to their detailed structural characterization. However, the use of these methods remains limited because the structure calculation algorithms have not been coupled yet to automatic minimization routines. Even when such a comprehensive modeling is not performed, the direct comparison between experimental XRD patterns and those calculated from the hypothesized structure is essential to assess the validity, and possibly the limits, of the proposed structure model.

In any case, the increased use of experimental XRD pattern modeling has led over the last few years to a significant improvement of our understanding of MLS structure at different scales. At the particle-scale, it was in particular possible to reconcile results obtained from XRD and SAXS by proposing a new model for stacking defects. It has also been shown that the nature of outer surface layers influences significantly the intensity distribution, especially for chlorite-rich samples, and that a complete structure characterization for such samples should include this parameter. In addition, this approach allowed reconsidering the actual nature of illite-smectite MLSs found in natural samples with the systematic presence of multi-component structures and/or of MLSs exhibiting a partial segregation of their elementary layers, and the existence of “unusual” MLSs. It has also been possible to refine the actual structure of MLS elementary layers. Additional fundamental findings will undoubtedly follow from the wider application of this approach to natural and synthetic samples. In particular new insight into the actual nature of reactions taking place in geological environments are expected.

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